On the Alkylation of Phenol with Primary Alcohols in the Presence of Aluminium Chloride

AUTHOR(S):

Shingu, Haruo; Matsushita, Hideo

64. On the Alkylation of Phenol with Primary Alcohols in the Presence of Aluminium Chloride.

Haruo Shingu and *Hideo Matsushita.*

With the view to introduce a normal alkyl side-chain into the aromatic, esp. phenolic, nucleus[1)2)3)] we have investigated the reaction between the phenol and the alcohol in the presence of anhydrous $AlCl_3$ in the following three ways:

1) The alcohol-$AlCl_3$ equimolecular complex had been previously prepared and was then treated with phenol and $AlCl_3$: the condensation without the additional $AlCl_3$ at 100°C. gave no reaction product, but at 150°C. gave 4% of n-butyl-phenol. The reaction with an addition of 1.0 mol. $AlCl_3$ at 120—130°C, 150°C. gave 24.0, 35.7% of n-butyl-phenol respectively.

2) The phenol-$AlCl_3$ equimolecular complex had been previously prepared and was then condensed with alcohol in the presence of $AlCl_3$ at 120—130°C for one hour: the reaction with 0.0, 0.5, and 1.0 mol. of the additional $AlCl_3$ yielded trace, 21.2%, and 15.1% of n-butyl-phenol, respectively.

3) The condensation between the previously prepared alcohol- and phenol-$AlCl_3$ complex in the presence of $AlCl_3$ at 120—130°C for several hours: the reaction with 0, 0.5 and 1.0 mol. of additional $AlCl_3$ gave 15.0, 36.7 and 23.3% of n-butyl-phenol, respectively.

The structure of the alkyl chain introduced by this method is confirmed from the consideration of the following facts: the butyl-phenol fractions obtained, b. p.$_{10}$ 110—113°C. and b. p.$_{10}$ 124—129°C. (o-isomer: b. p.$_{10}$ 110°C.[4)]; p-isomer: b. p.$_{10}$ 125—126°C.[4)]) are both liquid, and the benzoate derivative of the p-isomer (b. p.$_{10}$ 124—128°C.) melts at 26.5—27.0°C. (m. p. 27°C.[4)]). On the other hand, sec- and tert-butylphenol are crystals (m. p. 55°C. and 99°C. respectively).

Literatures

1) Ipatieff; J. Org. Chem., **5**, 253 (1940).
2) Tsukervanik; J. Gen. Chem., **7**, 623 (1937); C. A. **31**, 6778 (1937).
3) Smith; J. Amer. Chem. Soc., **56**, 1419 (1934).
4) Sandulesco; Bull. Soc. Chim., (4) **47**, 1300 (1931).

---

65. Catalytic Dehydrogenation of Aliphatic Primary Alcohol. (II)

Haruo Shingu and *Toyoji Tsuchihara.*

In the foregoing report on the investigation of dehydrogenation of isoamyl-alcohol over Cu, CuO-Cr_2O_3 and Cu-Cr_2O_3 catalysts, we concluded that these